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PART XI
ASTIA DOCUMENT No. AD 142115

MECHANISM OF RAIN EROSION

Part XI. Effect of Residual Stresses and of Molding Variables on the Erosion Resistance of Nylon

OLIVE G. ENGEL

NATIONAL BUREAU OF STANDARDS

NOVEMBER 1957

Statement A
Approved for Public Release

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WRIGHT AIR DEVELOPMENT CENTER

NOTICES

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NOVEMBER 1957

MATERIALS LABORATORY
CONTRACT NO. AF 33(616)-53-9
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WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
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FOREWORD

This report was prepared by the National Bureau of Standards under USAF Contract No. AF 33(616)-53-9. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials," Task No. 73400, "Structural Plastics." The project was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. George P. Peterson acting as project engineer.

The report covers the period of work from March 1955 to October 1956.

ABSTRACT

It is shown that residual stresses in the original plastic sheet material and the use of improper molding conditions for the fabrication of test specimens may provide an incorrect rain-erosion-resistance rating for the material in question and misleading evidence in regard to the failure mechanism of it. Test results indicate that properly molded nylon FM-10001, which was heat treated by the manufacturer to remove residual stresses in the plastic sheet, is one of the most rain-erosion resistant of the rigid plastic materials that have been evaluated at impingement velocities up to 600 mi/hr. This rigid plastic closely approaches the rain-erosion-resistance of neoprene elastomers at 600 mi/hr.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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MECHANISM OF RAIN EROSION

Part XI. EFFECT OF RESIDUAL STRESSES AND OF MOLDING VARIABLES ON THE EROSION RESISTANCE OF NYLON

1. Introduction

As has been pointed out before (1, 2, 3)[a] the erosion that is produced on any given structural material by high-speed waterdrop impingement is a direct consequence of the properties of a waterdrop during collision with a solid surface. Under impact conditions a waterdrop acts as though it were a hard sphere, but, unlike a sphere of hard material, it undergoes a high-velocity radial flow. The stresses that each waterdrop blow imposes are: (a) the compressive impact load that is exerted at the point of the collision, (b) the shear and tensile stresses that are exerted by the radial flow of the water, and (c) the moment of force that the radial water flow exerts against any protrusion of the solid material above the essentially planar surface. These properties of an impinging waterdrop are constant for all collisions that it undergoes with solid surfaces. If all solids had the same intrinsic properties, therefore, there would be only one way in which the solid material would respond to the stresses imposed by the waterdrop, and, consequently, only one mechanism of high-speed rain erosion.

Actually, there are as many mechanisms of high-speed rain erosion as there are broad groups of intrinsic properties in structural materials. This is because each material responds to the waterdrop stresses in a way that is determined by its own characteristic properties. In fact, the mechanism on two specimens of a given material may even be different if the properties of one of them have been modified with respect to the properties of the other. The possibility of such a modification in plastics materials is more immanent than it is in the case of metals. Plastics are readily subject to a change in properties as a consequence of changes in the temperature and pressure used to mold them. It is possible, therefore, that specimens that are molded from plastics sheet material may have properties that are different from those of the original sheet material. This, in fact, will be true in general unless the molding of the specimens is carried out under essentially the same conditions of temperature and pressure as the molding of the original sheet. If a difference in properties is produced during the forming

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[a]Numbers in parentheses indicate references at the end of this report.

operation, a test of rain erosion resistance of a plastics material as determined by use of a molded specimen will not be a true measure of the rain erosion resistance of the original material. How serious differences of this kind may become is a matter to be determined by experiment.

The results obtained in a preliminary study of the rain erosion mechanism of nylon, which are presented in this report, not only show that the problem exists but indicate the importance that it can have. By chance two sheets of nylon FM-10001 (now coded Zytel 101) were molded into airfoil-shaped specimens and tested for rain erosion resistance about ten months before the remaining sheets were molded into specimens and tested. All of the specimens that were molded and tested at the later time responded to high-speed rain impingement in a markedly different way from the specimens of the same material that were molded and tested earlier. Nevertheless, all of the sheet stock used to made the specimens at the two different times was originally obtained at the same time. Since no noticeable change occurs in the plastics material that was used as a result of storage for this length of time, the difference in the behavior of the specimens that were tested at the two different times is almost certainly a result of a change in the properties of the material due to a change in the conditions under which it was formed into specimens at the two different times.

2. Probable Rain Erosion Resistance of Nylon FM-10001

There are two possible solutions to the rain erosion problem: (A) rubbery materials that mitigate the stresses that the impinging waterdrops exert to the extent that the mitigated stresses are within the strength properties of the rubbery material, and (B) rigid materials that are able to sustain without failure the maximum unmitigated stresses that the impinging waterdrops are able to impose. As the impingement velocity is increased, a material that was a rubbery-material or a rigid-material solution to the rain erosion problem at a lower velocity will be eliminated as a rain erosion resistant material if its strength properties are exceeded at the higher velocity. For example, neoprene is a rubbery-material solution to the rain erosion problem at an impingement velocity of 500 mi/hr. Polymethyl - methacrylate in the form of Lucite or Plexiglas is not pitted at all after test in 1-in./hr rain for 19 hours at an impingement velocity of 200 mi/hr, but it is pitted in less than 1 min under the same conditions of rain density at an impingement velocity of 600 mi/hr(4). Therefore, polymethyl - methacrylate is a practical rigid-material solution to the rain erosion problem at an impingement velocity of 200 mi/hr, but it is completely eliminated as a rain-erosion resistant material at an impingement velocity of 600 mi/hr.

Nylon FM-10001 is a durable plastics material having a tensile strength of 10,500 psi, shear strength of 9,600 psi, ultimate elongation of 90%, and Izod impact strength of 1.0 ft lb/in. (5). It seemed possible that this nylon plastics might have strength properties close to the lower limit of those required for a rain-erosion resistant material of class (B) at an impingement velocity of 600 mi/hr. To determine the rain-erosion resistance of this material several 1/8-in. sheets of nylon FM-10001 were obtained from the E. I. du Pont de Nemours Company.

2.1 Resistance to Impingement with Oil-Filled Gelatin Capsules

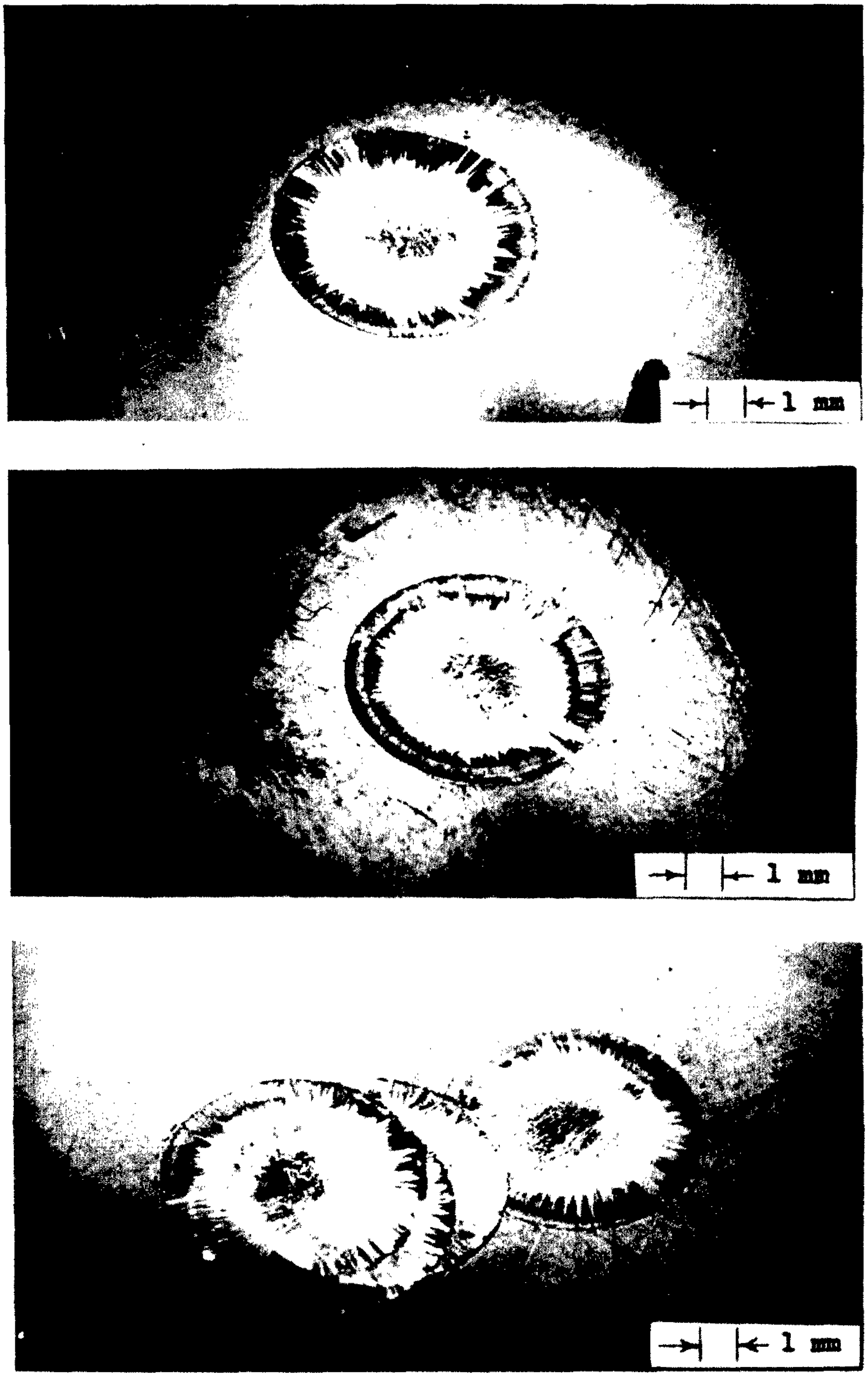
A test of this material was made using oil-filled gelatin capsules fired from a Benjamin air rifle. No characteristic marks at all were made on the surface of the nylon sheet by oil-filled gelatin capsules that impinged at a velocity of 900 ft/sec. Neoprene coatings, which constitute the presently accepted rubbery solution of the rain erosion problem at impingement velocities of 500 mi/hr, are damaged by the impingement of oil-filled gelatin capsules at a velocity of 900 ft/sec.

2.2 Resistance to Impingement with Deforming Lead Pellets

A test of the nylon sheet was also made using deforming lead pellets that were fired from the Benjamin air rifle. Deforming lead pellets that were fired against it at velocities of 490 ft/sec, 530 ft/sec, and 640 ft/sec left small circles of abrasion but produced no cracks. See Figure 1. No cracks were produced even on multiple impingement with lead pellets at a velocity of 490 ft/sec. See Figure 1(c). Inspection at X62.5 magnification of the structure of the dim circle made at the impingement velocity of 530 ft/sec showed that it consisted of very fine lines in the radial direction. See Figure 1(a). These lines may have been caused by the drag of the deforming lead over the surface of the nylon as the lead pellet flowed radially during the collision. The damage mark made in the nylon by a deforming lead pellet at an impingement velocity of 640 ft/sec consisted of a very shallow depression and a circle of abrasion. See Figure 1(b). In the case of neoprene coatings, the damage produced by the impingement of deforming lead pellets often consists of a circular cut surrounded by a coating-bubble.

3. Rain Erosion Test of Nylon FM-10001

Three separate studies of the rain erosion resistance of this plastic material have been made. The results of these



(a) VELOCITY 530 ft/sec

(b) VELOCITY 640 ft/sec

(c) VELOCITY 490 ft/sec

FIGURE 1. SINGLE AND MULTIPLE SHOTS ON NYLON FM-10001 WITH DEFORMING LEAD PELLETS

studies in the chronological order in which they were made are reported in the following sections. The studies are designated as Study I, Study II, and Study III, respectively.

3.1 Results of Study I

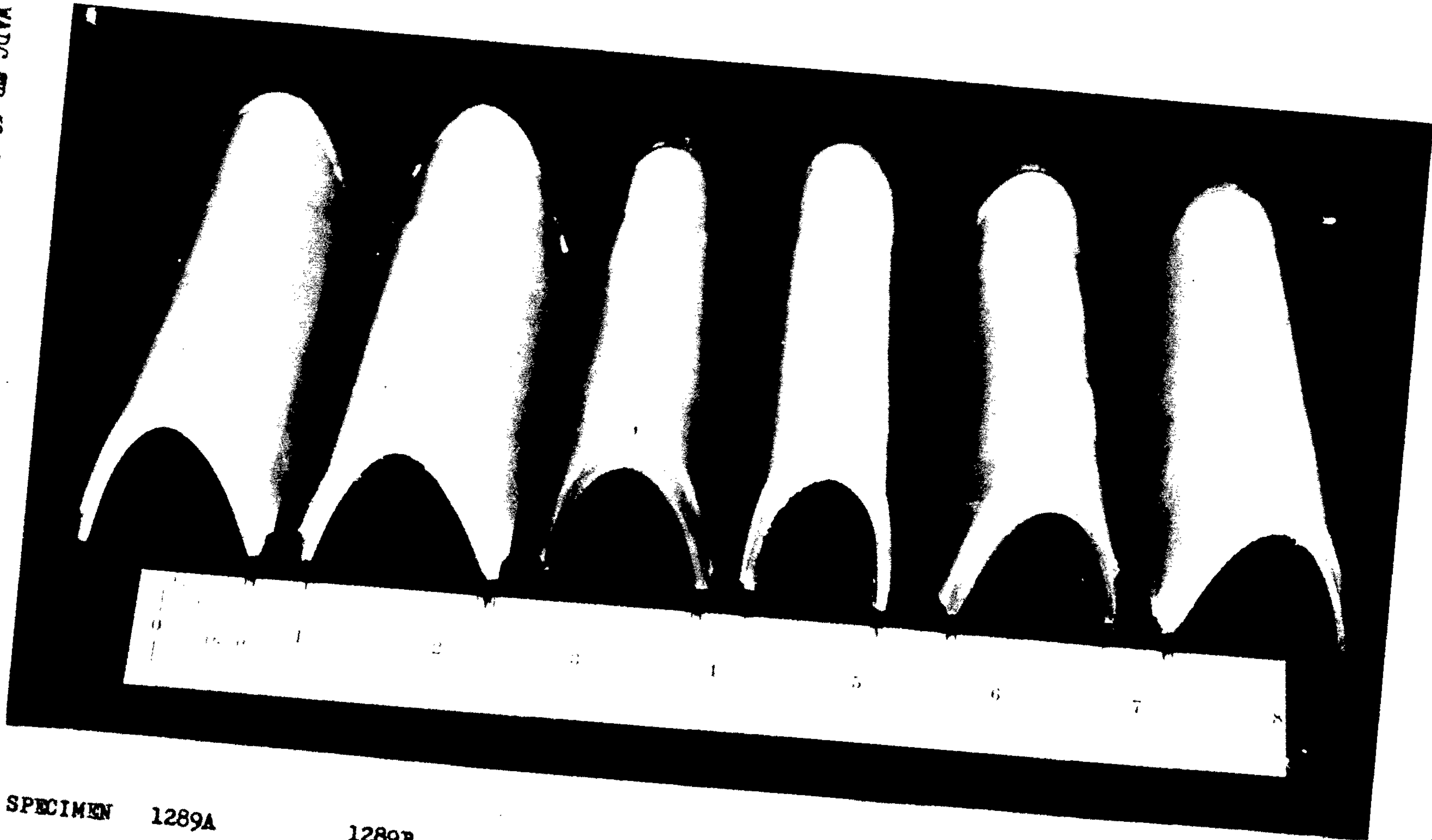
Before the tests with oil-filled gelatin capsules and with deforming lead pellets were made, two of the 1/8-in. sheets of Nylon FM-10001 were sent to the Cornell Aeronautical Laboratory to be molded into rain erosion specimens. No molding instructions were specified. The two specimens that were made from this material were given the numbers 1289A and 1289B at that laboratory. The specimens are shown in Figure 2. These specimens were tested for rain erosion resistance on the Cornell Aeronautical Laboratory rotating arm at a velocity of 600 mi/hr in 1-in./hr simulated rain. Specimen Specimen 1289A was tested for 25 sec and specimen 1289B was tested for 1 min. The visual appearance of these specimens was reported (6) in tabular form in the way given in Table 1. The specimens were forwarded to the National Bureau of Standards for study.

Table 1.

Reported Rain Erosion Results of Study I

Specimen Number	Material	Length of Exposure	Visual Appearance
1289 A	Nylon	25 sec	Very fine pitting along leading edge.
1289 B	"	1 min	Several pits near center of leading edge.

Visual comparison of these specimens with a piece of the original nylon sheet material showed that both specimens had acquired a slight yellow color. Specimen 1289A was discolored more than specimen 1289B; they had Munsell color designations of 5.0 Y 7.6/4 and 5.0 Y 8/2.4, respectively. See Table 3, page 11. The color change indicates that the plastics material was modified during molding and that, consequently, its properties were changed. Abrasion of one end of specimen 1289A with a file, and with emery and sand paper, removed a considerable amount of the color. This appeared to indicate that the major part of the color change was at the surface of the specimen where it had been in contact with the surface of the mold during the forming operation.



SPECIMEN	1289A	1289B	1345A	1345B	1346A	1346B
TEST TIME	25 sec	1 min	5 min	15 min	20 min	30 min

FIGURE 2. SPECIMENS OF NYLON FM-10001 AFTER VARIOUS TEST INTERVALS. STUDY II.

In addition to the color change, both specimens had apparently also changed contour due to creep since they were formed. Whereas the outer distance from side to side at the base of a Cornell Aeronautical Laboratory rain erosion specimen should measure 1 in., specimen 1289A measured 1-7/16 in., and specimen 1289B measured 1-1/2 in. See Figure 2. Possible explanations of this creep are that the innermost layers of the nylon had not reached a sufficiently high temperature for forming at the time that the specimen was molded with the result that these layers were forced into shape, and (or) that insufficient time was allowed for the polymer chains to move into new positions in the molded specimen. Tensile stresses may have formed across the outside curve of the specimen and compressive stresses across the inside curve of it. See Figure 3(a). In terms of the microscopic picture, the polymer chains may have become stretched across the outside curve of the specimen and bunched across the inside curve of it. These stresses would act together to cause deformation of the specimen. See Figure 3(b). The fact that these specimens developed a yellow color indicates that the mold was actually too hot for forming this material. If the first possible explanation of the creep of the specimens is correct, the specimens must have been molded and cooled rapidly before temperature equilibrium was established throughout the thickness of them in order to explain how the inner layers could have been molded below the correct forming temperature at the same time that the outer layers suffered a modification of properties due to excessive heating. If the molding and subsequent cooling of the specimens was carried out very rapidly, the second possible explanation of the creep of the specimens may also be partly a correct explanation of their change in shape after forming.

Inspection of specimen 1289A and 1289B at X25 magnification revealed that specimen 1289A was more severely damaged after test for 25 sec than specimen 1289B was after it was tested for 1 min under the same conditions of velocity and rain rate. This paradoxical result is in agreement with the observation that specimen 1289A had suffered the most extensive color change during molding. It was observed that the leading edge of specimen 1289A was checked with closely spaced cracks. The cracks were, in general, essentially parallel to one another; connecting cracks also were evident; material had chipped away along cracks and between cracks. This crack structure existed on the leading edge and extended a short distance down each side of the specimen. See Figure 3(c). The more or less parallel cracks did not run along the length of the specimen but were oriented at an angle across the leading edge. Observation of the crack structure down the length of the

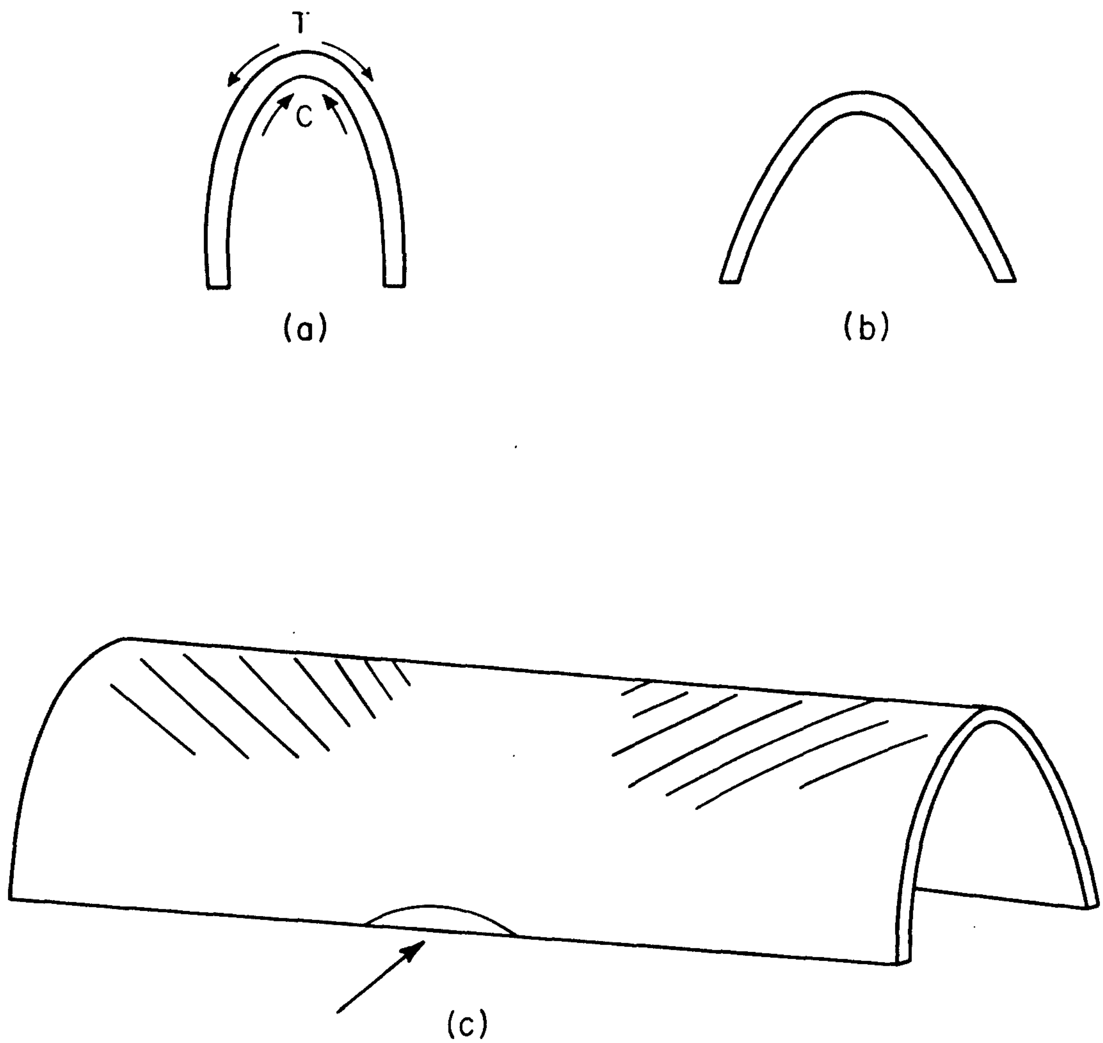


FIGURE 3. (a) SCHEMATIC REPRESENTATION OF TENSILE (T) AND COMPRESSIVE (C) STRESSES MOLDED INTO A RAIN EROSION SPECIMEN

(b) RELAXED STATE OF THE SPECIMEN AFTER CREEP HAS OCCURRED

(c) LOCATION OF STRESS CRACKS WITH RESPECT TO THE POSITION OF THE ORIFICE (ARROW) THROUGH WHICH THE ORIGINAL NYLON SHEET WAS INJECTION MOLDED specimen revealed that it disappeared in the center of the specimen but that it could be observed again at the opposite end of it. The angle at which the cracks were oriented with respect to one another at the two ends of the specimen was about 90 degrees. The existence of erosion along cracks and between cracks seems to indicate that the cracks were there during part or during all of the time that the specimen was under test on the rotating arm.

The nylon sheet from which the rain erosion specimens were prepared was a circular plate formed by injection molding. There was a raised disk of the nylon plastics in the center of the circular plate at the point where the molten material had been forced through an orifice to form it. It was later observed that a vestige of this disk remained in the form of an outline of it at the extreme side of specimen 1289A. This outline is indicated with an arrow in Figure 3(c). Consideration of radial lines from the point at which the molten nylon was injected to form the original circular plastics sheet suggests the thought that the parallel cracks observed on the rain-eroded specimen may bear some relation to them; it suggests the thought that the more or less parallel cracks observed on specimen 1289A were produced as a consequence of residual stresses in the original sheet material. If the molten nylon was injected into a cold mold, concentric circles of stress around the point at which injection occurred may have been frozen in it. In the light of this possibility, the more or less parallel cracks may be a type of stress-crazing. It is possible that the cracks in specimen 1289A formed when the specimen was cooled after being molded. In this case they were present before rain impingement against the specimen took place during test on the rotating arm apparatus. On the other hand, they may not have formed until the impact load of the impinging waterdrops was applied.

Inspection of specimen 1289B revealed random scratches and possible evidence of abrasion on the surface but no crack structure at all such as was observed on specimen 1289A. Furthermore, similar defects could be observed on the side of the specimen which was protected from direct collisions with the rain. Hence, they may not even have been caused by waterdrop impingement. It is noteworthy, however, that the inner surface of scratches on the leading edge had begun to show signs of erosion. This specimen also contained an outline of the originally raised disk of plastics that had marked the location of the orifice through which the sheet of nylon from which it was prepared had been injection molded. An attempt was made to induce crack formation on this specimen by exposing it to ultraviolet light. The specimen was placed 8 in. below a 275-watt RS Westinghouse sunlamp and was irradiated for approximately 5 hours. The specimen was then brought to within 5 in. of the lamp, and irradiation was continued for an additional 6-1/2 hours. During the test the specimen was kept as cool as possible with an electric fan to prevent annealing the cracks if they should form. At the end of the test, examination of the specimen at X25 magnification failed to reveal any crack structure at all.

3.2 Results of Study II

About ten months later, additional sheets of nylon FM-10001, which had been obtained at the same time that the sheet material used for Study I was obtained, were sent to Cornell Aeronautical Laboratory to be fabricated into rain erosion specimens that were to be tested for more extended periods of time. At this time it was strongly suspected that nylon would prove to have a high order of rain erosion resistance because of its resistance to impingement with oil-filled gelatin capsules and with deforming lead pellets and that it might constitute a rigid-material solution of the rain erosion problem up to an impingement velocity of about 600 mi/hr. No molding instructions were forwarded with the plastic material. At the Cornell Aeronautical Laboratory the specimens that were made from this material were given the numbers 1345A, 1345B, 1346A, and 1346B. They were tested on the rotating arm for 5 min, 15 min, 20 min. and 30 min, respectively, at the same velocity (600 mi/hr) and in the same density of artificial rain (1 in./hr) as was used for specimens 1289A and 1289B of Study I. The appearance of these specimens after test was reported (6) in tabular form in the manner given in Table 2. The specimens were forwarded to the National Bureau of Standards for study.

Table 2.

Reported Rain Erosion Results of Study II.

Nylon	Length of Test	Appearance of Specimen after Test
C.A.L. No. 1345 A	5 min	Numerous shallow pits on leading edge
1345 B	15 min	More concentrated and deeper pitting
1346 A	20 min	Deep, heavy pitting along leading edge
1346 B	30 min	Eroded through 0.060-0.080 in. of leading edge thereby weakening specimen

Visual inspection of these specimens provided the following information. All four of the specimens had become discolored during molding, three of them were strongly discolored. The Munsell color designation was determined for each of the specimens. These color designations are given in Table 3.

Table 3.

Color Developed in Specimens of Nylon FM-10001 During Forming, Study I and Study II

Specimen Number	Munsell Color Designation		I.S.C.C. Color Designation
1289A	5.0 Y	7.6/4	weak yellow
1289B	5.0 Y	8/2.4	weak yellow
1345A	10 YR	5.4/6	moderate yellowish brown
1345B	5.0 Y	7.5/4	weak yellow
1346A	2.5 Y	5.4/4	moderate yellowish brown light olive brown
1346B	7.5 Y	7.4/2.8	weak yellow

In addition, three of the specimens had changed contour due to creep since the time that they were formed. Only specimen 1345B retained the 1-in. chord dimension of a Cornell Aeronautical Laboratory rain erosion specimen. See Figure 2.

Contrary to expectations, all of these specimens were in a serious state of damage. Each contained a wide swath of erosion down the full length of the leading edge. The exposed underlying layers of the material were close to the original color of the nylon. As in the case of specimen 1289A of Study I, this indicates that excessive heating during molding was restricted to the layers at or close to the surface.

Specimen 1345A was tested for 5 min. The outer distance from one side to the other at the base of this specimen had increased from the original 1 in. to 1-1/4 in. The surface layers of the entire specimen had turned from the ivory color of the original plastics sheet to a distinct light brown due to excessive heating during forming. A swath of severe erosion damage ran along the leading edge from one end to the other of the specimen. The erosion in this swath, which was nearly 1/2 in. wide, was advanced but appeared to be of a finer texture than that on the specimens that were eroded for longer periods. On one side of the swath of erosion an area existed from which the brown surface layer only had chipped off. The surface of this area had a smoothness about comparable to that of frosted glass.

Scrutiny at X25 magnification of the brown surface along the fringe of the swath of erosion damage showed that the same type of crack structure existed as was observed on specimen 1289A. The center of the specimen was also found to be without such cracks, and the angle at which the cracks had formed with respect to one another at the two ends of the specimen was again about 90 degrees. See Figure 3(c). The outline of the originally raised disk of plastics that had marked the point at which the molten nylon had been injected into the mold to form the circular sheet from which the specimen was made was also visible at the base of the specimen. The crack formation was qualitatively along radii from this point, as was observed in the case of specimen 1289A.

At the border of the swath of damage down the leading edge of the specimen 1345A, rain erosion was observed along cracks and between cracks at the ends of the specimen where cracks existed. The erosion appeared to consist of material chipped off the surface, as in the case of specimen 1289A of Study I. At the center of the specimen, where a tier of cracks did not exist, the border of the damage swath down the leading edge of the specimen was simply irregular. Apparently, even where the surface was not weakened by the existence of the more or less parallel stress or craze cracks, the brittle brown surface layer chipped off anyway. This may indicate that embrittlement of the surface layer caused the initial failure of the specimen and that the effect of crazing, produced by stresses in the original plastics sheet, may only have been a contributing factor to the observed damage. The chipping off of the brittle surface layer by the impinging waterdrops produced a roughened surface. Depressions in the roughened surface almost certainly served as pressure multipliers for succeeding waterdrop blows (1) and hence reduced the possibility that the underlying layers of material would be able to withstand the erosion attack.

Specimen 1345B was tested for 15 min. It was the only nylon specimen that did not change shape due to creep. See Figure 2. The surface layers of this specimen along the leading edge and to a distance about half-way down the sides of the specimen had been discolored to a light tan by superheating during molding. However, a large part of the embrittled tan layer had been removed by the waterdrop impingement of the rain erosion test, and only the fringes of it remained about half-way down each side. The large areas from which the tan embrittled layer had been removed were light colored. They were smooth, but dull, and felt like frosted glass.

Severe erosion was restricted to a narrow band down the center of the swath from which the tan embrittled layer had been removed. The outline of the originally raised disk of plastics, which had marked the location of the orifice through which the nylon had been injected into the mold to form the sheet from which this specimen was made, could be seen at the edge of one side of the specimen. See Figure 3(c). A very close-spaced crack formation that was oriented at an angle to the length of the specimen was present at each end of it. The cracks were roughly along radii from the point at which the plastics sheet was injection molded. Crack formation also existed at the center of the specimen. The direction of cracks at this location was roughly parallel to the length of the specimen. Deep cracks had started to form in the plastics at each end of the specimen. Another short deep crack could be seen about an inch from one end. The additional 10 min of test that this specimen was given over specimen 1345A had served to widen both the swath of severe damage and the swath from which the tan embrittled layer of plastics was removed; it had also made the severe damage more acute.

Specimen 1346A was tested for 20 min. It had changed shape due to creep since it was formed so that the 1-in. distance from side to side of the specimen had increased to 1-1/4 in. See Figure 2. The entire surface of the specimen was a strong tan or light brown color. It was, however, not quite as dark as specimen 1345A. The glossy tan surface layer was removed by waterdrop impingement during the rain erosion test from an approximately 3/4-in. swath down the length of the specimen on the leading edge. Severe erosion, which had progressed further than on specimen 1345B, was restricted to the center of this swath. The light-colored plastics along the boundaries of the swath from which the embrittled tan layer had been removed had a dull but relatively smooth surface as on specimens 1345A and 1345B. The outline that remained of the originally raised disk of plastics, which marked the location of the orifice through which the original plastics sheet had been injection molded, could be seen on the inner surface at the edge of one side. The same type of stress-crack formation could be seen as that observed on specimens 1289A, 1345A, and 1345B. At one end of this specimen stress-cracks could be seen in a narrow band which had been protected from the rain impacts. This band extended across the leading edge. This observation indicates that the stress-cracks were present before the specimens were tested.

Specimen 1346B was tested for 30 min. It resembled specimens 1289A and 1289B in that it had changed shape extensively by creep and in that it was discolored only to a pale yellow. It differed widely from these specimens, however, in the extent to which it was damaged by the waterdrop impingement. The glossy surface layer was removed from a swath that extended down the length of the specimen on the leading edge and that, at the high-speed end, was about an inch in width. A swath of very severe damage which was about 1/2 in. wide ran down the center of the swath from which the glossy surface layer was removed. The outline of the originally raised disk, which marked the location of the orifice through which the sheet of nylon had been injection molded, was on the inner surface of the specimen at the edge of one side. Examination of the specimen at X25 magnification revealed crack formation similar to that which was observed on all of the other nylon specimens of Study I and Study II with the exception of specimen 1289B.

The specimens of Study II were weakened toward erosion attack in three ways. First, they were molded from sheet material that contained residual stresses; the result of this was stress-crazing in the surface of the specimens. Secondly, the color change on the surface of these specimens indicates that they were exposed to excessive heating during forming, making it possible that the surface layers possessed properties different from those of the high strength nylon FM-10001 plastics; embrittlement of the surface layers may have resulted so that these layers may have been more easily subject to being cracked or chipped away from the remainder of the specimen in the same way that a thin brittle coating applied to a rain erosion specimen-base is chipped away. Finally, tensile and compressive stresses were molded into the specimens as is indicated by their deformation. If the surface layers contain internal tensile stresses during the rain erosion test, they are subject to higher stresses than unstressed material would be during test.

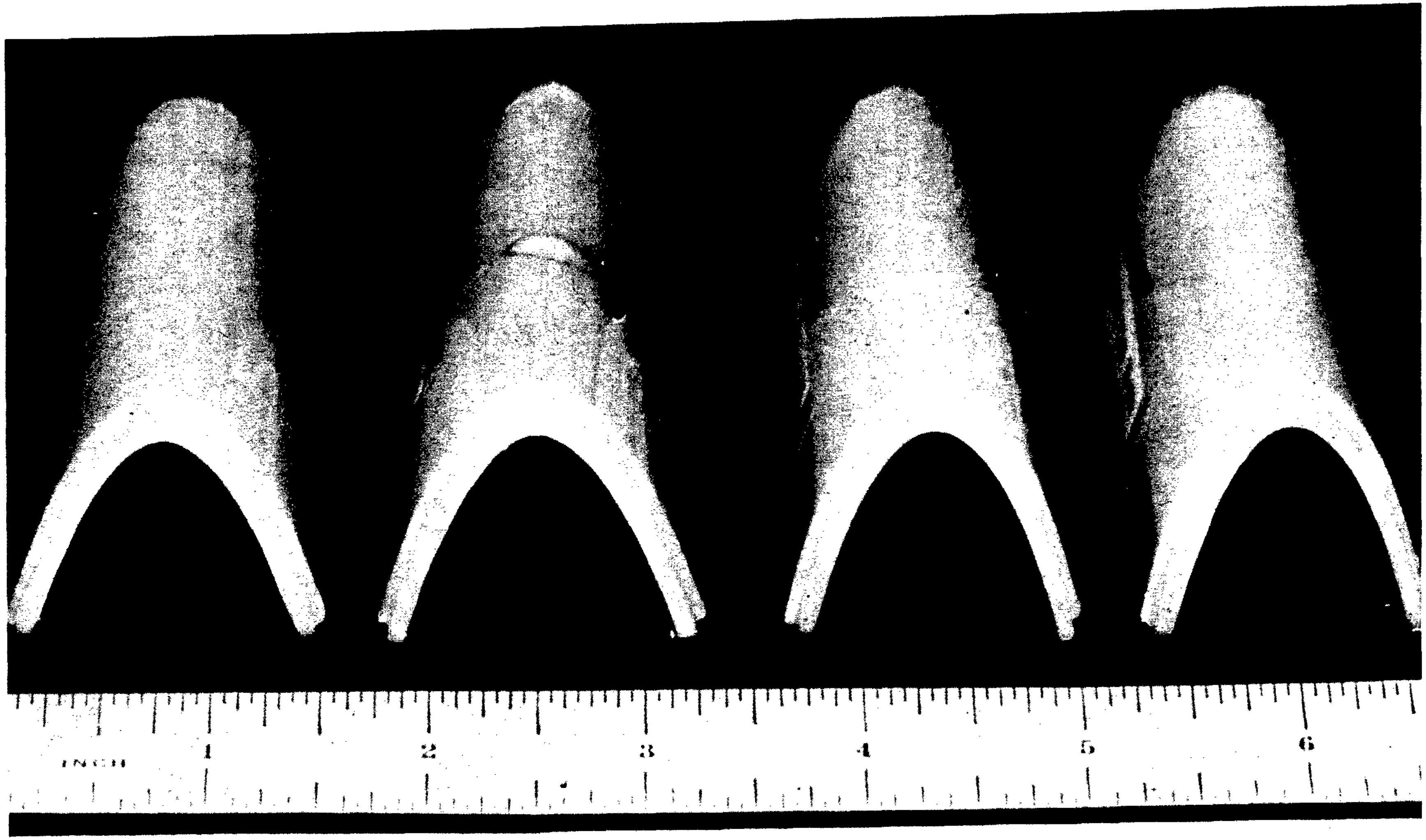
The compressive, tensile, and shear stresses exerted by the impinging waterdrops produced the erosion damage that was observed. The localized pressure loads of the impinging waterdrops would tend to fracture a thin brittle surface layer and the very rapid radial flow of water from the impinging drops would exert a force against the edges of fracture or craze cracks that would tend to rip material out of the surface. Even though the material that was exposed after the deteriorated surface layer was removed may have had properties close to those of the original nylon plastics, it was weaker toward the erosion attack than the original nylon surface would have been because it was rough; surface pits and crevices are pressure-multipliers to impinging water masses. Surface material that was under tension would tend to fracture under the tensile load exerted by the collision and radial flow of the individual drops.

It is important to realize that the weaknesses that have been referred to are not characteristic of nylon FM-10001 itself but are the result of residual stresses and of molding variables. Consequently, these modes of failure may be fictitious as far as properly molded nylon FM-10001 itself is concerned.

3.3 Results of Study III

More nylon FM-10001 sheet material was secured from the E. I. du Pont de Nemours Company. The new material consisted of four injection molded 1/8-in. oblong plaques that were 4 in. by 8 in. in size. These plaques were heat treated at the source. Molding instructions for this material, obtained from the manufacturer, were that the plaque was to be heated in oil or in Glyco wax S-932 to a temperature of 350 to 400°F; when the plaque became soft it was to be removed from the hot bath and formed. The nylon sheet material and the manufacturer's molding instructions were sent to the Cornell Aeronautical Laboratory where four airfoil-shaped specimens were prepared. The material was heated in oil at 400°F, and the specimens were formed in a matched metal mold that was held at the same temperature. The mold was kept closed with no pressure and was allowed to cool slowly to room temperature before the nylon specimens were removed. These specimens were given the numbers 1495A, 1495B, 1496A, and 1496B at the Cornell Aeronautical Laboratory. They were tested on the rotating arm at a velocity of 600 mi/hr in 1-in./hr artificial rain for 25 sec, 1 min, 5 min, and 30 min, respectively. Three flat specimens that measured 3-5/8 in. by 1/2 in. were also cut from this 1/8-in. nylon sheet material. They were given numbers 1497A, 1497B, and 1497C and were tested in the as-received state under the same conditions of velocity and rain rate for 25 sec, 1 min, and 5 min, respectively. The fact that these specimens were tested was reported (6); the visual appearance of the individual specimens after test was not given. The specimens were returned to the National Bureau of Standards for study.

These specimens retained the original color of the nylon sheet material from which they were formed except for specimen 1495B which had turned a very pale yellow. The specimens had changed shape, however, due to stresses that were molded in them. The 1-inch distance from side to side of a Cornell Aeronautical Laboratory rain erosion specimen had increased to the following sizes: specimen 1495A, 1-1/2 in.; specimen 1495B, 1-1/2 in.; specimen 1496A, 1-3/8 in.; and specimen 1496B, 1-3/8 in. The specimens are shown in Figure 4. An extraneous damage mark can be seen on specimen 1495B. This damage was encircled with crayon at the Cornell Aeronautical Laboratory and marked to be disregarded as far as erosion damage was concerned.



SPECIMEN	1495A	1495B	1496A	1496B
TEST TIME	25 sec	1 min	5 min	30 min

FIGURE 4. SPECIMENS OF NYLON FM-10001 AFTER VARIOUS TEST INTERVALS. STUDY III.

Microscopic examination of the original nylon sheet material revealed some scratches, a scattering of very fine blemishes, which may be pits or depressions, and a few larger spots which may be very small areas of mechanical abrasion. It is possible that the molten nylon replicated the surface of the mold in which the original plaque of material was formed, and (or) suffered some mechanical abrasion in the ordinary course of handling.

Microscopic examination of the flat specimen, 1497A, and of the airfoil-shaped specimen, 1495A, which had each been tested for 25 sec, produced the following observations. There were spots of etching on specimen 1497A, and scratches on the surface of this specimen were beaded with etch pits. In general, the density of fine blemishes and the number of scratches were greater on this specimen than on the original plastics sheet material. The surface of the leading edge of the airfoil-shaped specimen, 1495A, was more heavily etched than that of the flat specimen, 1497A, which was tested for the same length of time under the same conditions of velocity and rain rate. Spots of etching were more numerous on specimen 1495A than on specimen 1497A. This agrees with the observation that specimen 1497A was essentially as smooth to the touch as the original nylon sheet material, but the surface of the leading edge of specimen 1495A was roughened to the touch.

Specimen 1495A, which was molded under conditions specified by the manufacturer out of sheet material that had been given prior heat treatment to remove residual stresses, should be compared with specimen 1289A of Study I which was tested under the same conditions of impingement velocity and rain rate for the same length of time. Specimen 1289A contains stress cracks between which surface material has already chipped away. Specimen 1495A has suffered no such damage.

Microscopic examination of the flat specimen, 1497B, and of the airfoil-shaped specimen, 1495B, which had each been tested for 1 min produced the following observations. There was very little difference in the degree of etching on specimen 1497B, which had been tested for 1 min, and on specimen 1497A, which had been tested for 25 sec under the same conditions of velocity and rain rate. There was also very little difference in the appearance of the surface of the leading edge of the airfoil-shaped specimens, 1495B and 1495A, which had been tested for 1 min and for 25 sec, respectively, under the same conditions of velocity and rain rate. Specimen 1495B was smoother to the touch than specimen 1495A, although it had undergone test for twice as long.

Specimen 1495B, which was molded under conditions specified by the manufacturer out of sheet material that had been given prior heat treatment to remove residual stresses, should be compared with specimen 1289B of Study I, which was tested under the same conditions of velocity and rain rate for the same length of time. There is little difference in the extent of rain erosion damage on these two specimens. As was noted in Section 3.1, specimen 1289B was for some reason exceptional in that no stress cracks formed on it. Specimen 1289B had apparently been molded under temperature conditions that were nearly correct, for the color of this specimen was only very slightly different from that of the original nylon sheet.

Microscopic examination of the flat specimen, 1497C, and of the airfoil-shaped specimen, 1496A, which had each been tested for 5 min produced the following observations. There were scratches on specimen 1497C that were heavily etched with fine pits; there were quite a few spots that might be clusters of etch pits. In general, the density of background etching on specimen 1497C, the flat specimen which was tested for 5 min, was greater than that on specimen 1497B, the flat specimen which was tested for 1 min. This is in agreement with the observation that specimen 1497C was slightly roughened to the touch, whereas specimens 1497A and 1497B were essentially as smooth to the touch as the original nylon sheet material. On the surface of the leading edge of the airfoil-shaped specimen, 1496A, which was tested for 5 min, the scratches were more heavily etched with pits and there was a greater density of clusters of etch pits then on the surface of the leading edge of the airfoil-shaped specimen 1495B, which was tested for 1 min under the same conditions of velocity and rain rate. Specimen 1496A was as smooth to the touch as specimen 1495B and smoother than specimen 1495A.

Specimen 1496A, which was molded under conditions specified by the manufacturer out of sheet material that had been given prior heat treatment to remove residual stresses, should be compared with specimen 1345A of Study II which was tested under the same conditions of velocity and rain rate for the same length of time. The difference in rain-erosion damage done to these two specimens is remarkable. To visual inspection, specimen 1496A is undamaged, whereas specimen 1345A is in an advanced stage of erosion and contains a crack at one end that extends completely through the 1/8-in. thickness of the specimen. At the end of the 5-min interval of test, the effect of stresses in the original sheet material and the use of improper molding conditions in forming the test specimens is very remarkable. See Section 4 for photographs of these specimens.

As far as visual inspection is concerned, the surface of the airfoil-shaped specimens 1495A, 1495B, and 1496A, which were tested for 25 sec, 1 min, and 5 min, respectively, retained the glossy appearance of the original nylon sheet material. The surface of the leading edge of the airfoil-shaped specimen 1496B, which was tested for 30 min, was dulled to the unaided eye and was as rough to the touch as very fine sand paper. Microscopic inspection of this specimen showed that shreds of surface material were scuffed up on the leading edge; in many cases the material pulled up appeared to be hair-like tendrils of nylon. There were also clusters of very shallow pits on the leading edge of this specimen. There was still some gloss to the surface between these broken out spots. Various sizes of smaller shallow pits existed between the larger ones. At what must have been the high-speed end of the specimen, the broken out areas were almost merged or continuous, that is, very little space existed between them. In general, the broken out spots appeared to be preferentially elongated in the direction across the leading edge.

Specimen 1496B, which was molded under conditions specified by the manufacturer out of sheet material that had been given prior heat treatment to remove residual stresses, should be compared with specimen 1346B of Study II which was tested under the same conditions of velocity and rain rate for the same length of time. The difference in the rain-erosion damage done to these two specimens is astonishing. After the 30-min test interval at a velocity of 600 mi/hr in 1-in./hr artificial rain, specimen 1496B had suffered only a mild surface abrasion, but specimen 1346B was in a very serious state of damage. The erosion on specimen 1346B had cut through approximately half the total thickness of the specimen. See Section 4 for photographs of these specimens.

In the following paragraphs the development of the microscopic appearances on the specimens of Study III will be interpreted in terms of what may constitute the mechanism of erosion on nylon FM-10001. The surface of the original sheet material from which the test specimens were prepared contained very fine blemishes which may be replicas of similar defects in the surface of the mold that was used to make it. The surface of the original sheet material also contained scratches which were probably acquired during handling. There were more scratches and small blemishes on the specimen after 25 sec of test than there were on the original sheet material, and scratches could be seen that were beaded with etch pits. The test specimens were handled more than the pieces of original sheet material that were retained at the National Bureau of Standards and consequently could have acquired more scratches than were originally present on the nylon sheet from which they were made. The etching along scratches and at small isolated spots may not represent a real additional damage due to waterdrop impingement; it may be due simply to the wash-away of loose particles in the scratches and in small mechanically abraded areas which already existed on the specimen at the time that it was tested. This thought is substantiated by the fact that after 1 min of test the amount of etching was about the same as after 25 sec of test.

If real erosion damage did not occur within the first minute of test, evidence of it existed at the end of the first 5-min interval of test. After 5 min of test, the scratches were more etched out than after 1 min (or after 25 sec) of test. There were quite a few spots that appeared to be clusters of etching, and the density of background etching was greater than it was after 1 min of test. At the end of 30 min of test, the airfoil-shaped specimen was peppered with spots from which material was broken away to form shallow depressions. These broken out spots may have resulted from a deepening and widening of clusters of etching which formed around defects that were originally present in the surface of the specimen. On the other hand, there is some evidence that very short fine cracks or fractures may have formed in the surface and that thin layers of the surface material may have been peeled back from them. The fact that no cracks formed in the surface of the nylon even from multiple impingement with lead pellets throws the second explanation in question. More evidence is needed. The shots with lead pellets were repeated on a piece of the original nylon sheet that had been obtained for Study III and that had been heat treated by the manufacturer. Inspection of these damage marks indicated that no cracks had been produced. There was some evidence that the radial flow of the lead pellets may have scuffed up a very thin layer of the surface material. The observations that have been made on the eroded specimens indicate that the attack is real. It appears to be more nearly a consequence of the radial flow of water from the impinging drops than a result of the impact load that they exert. It would appear as though the attack is directed first to scratch and abrasion blemishes which are present on the specimens before the test is started; after tendrils of nylon are scuffed up from the surface, the radial flow of water from the impinging drops probably exerts a force against these vulnerable protruding structures.

It is possible that the airfoil-shaped specimen was somewhat more susceptible to erosion than the flat specimen. Greater damage on these specimens could have resulted from the presence of stresses that were molded in them. This thought is in agreement with the observation that on the airfoil-shaped specimen that was tested for 30 min the broken out spots appeared to be preferentially elongated in the direction across the leading edge, although the experimental observation could be equally well explained by the fact that the water flow is in the two directions perpendicular to a line down the center of the leading edge. It is also possible that fewer drops may actually have impinged against the flat specimen than against the airfoil-shaped specimen that was tested for the same length of time. The three flat specimens and the airfoil-shaped specimen that was tested for 5 min are shown in Figure 5. The lighting of the specimens in these views, which were taken at about the center of the specimen, does not show the microscopic damage that has been described. The pictures of Figure 5 do show, however, that no obvious damage was done to the specimens by waterdrop blows that were dealt at a velocity of 600 mi/hr for the test times indicated.

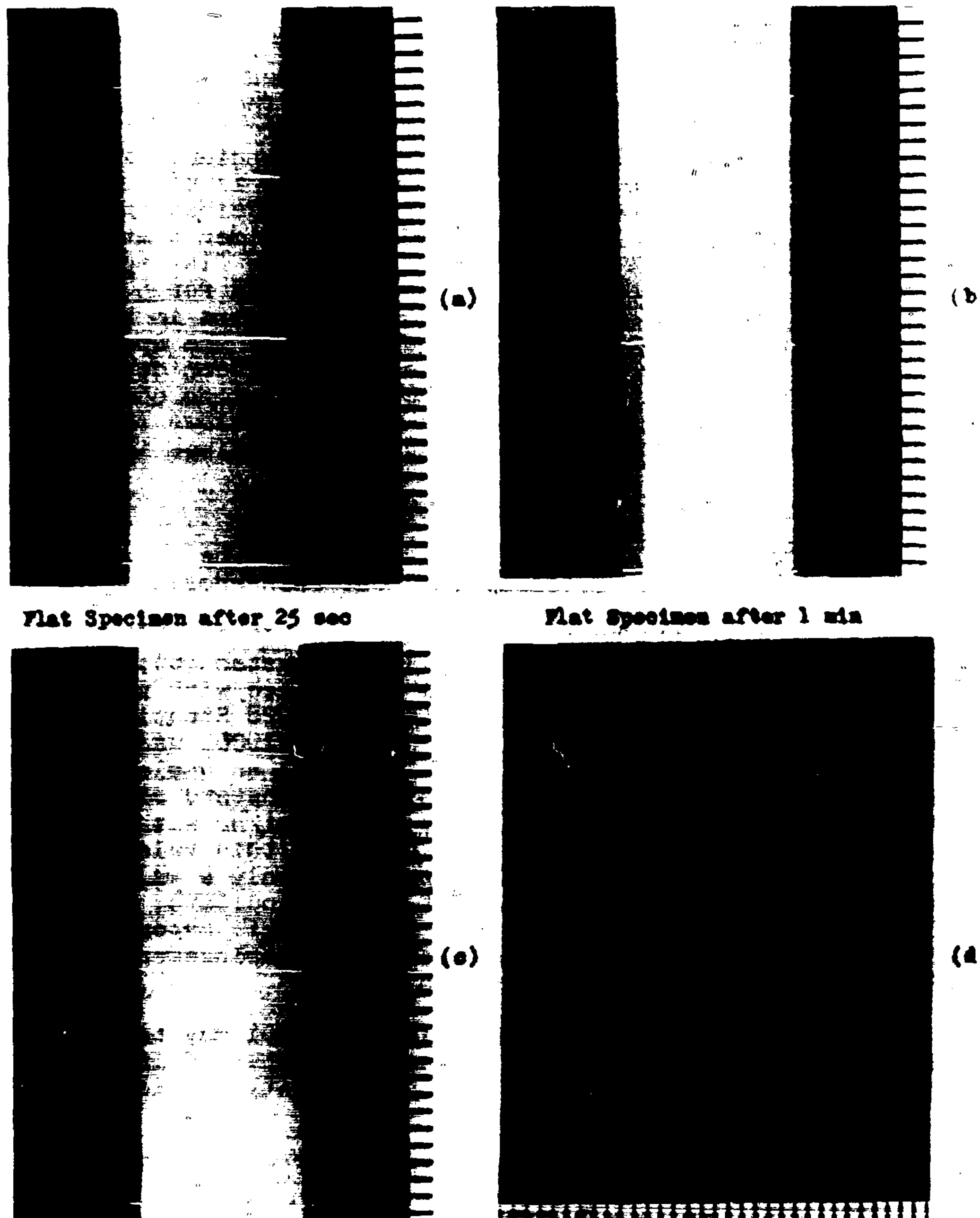
3.4 Rain-Erosion Resistance of Nylon FM-10001

From the test results of Study III it can be concluded that nylon FM-10001 is probably the most rain-erosion resistant rigid plastics material at an impingement velocity of 600 mi/hr that has been tested to date. It is more erosion resistant than the glasses that have been tested (6); it appears to be comparable in erosion resistance with Alsimag 228 Steatite (6). The glasses and Alsimag 228 Steatite were tested at a velocity of 500 mi/hr; nylon FM-10001 was tested at a velocity of 600 mi/hr. It appears than an unblemished surface of nylon FM-10001 may be able to withstand single waterdrop blows dealt at a velocity of 600 mi/hr without any damage at all. Multiple waterdrop blows at this velocity sustained over a period of 30 min produced only a mild abrasion of the surface. This test result indicates that nylon FM-10001 is a close approach to the rigid-material solution of the rain-erosion problem at an impingement velocity of 600 mi/hr. See Section 2.

It can be anticipated that nylon FM-10001 may be put into a form that is even more erosion resistant than is indicated by the results of Study III. This possibility is discussed in Section 4.

4. Importance of Residual Stresses and of Molding Variables on the Erosion Resistance of Nylon

Rain erosion damage is the direct result of the properties of a waterdrop during high-speed collision with a solid surface. The waterdrop acts as though it were a hard sphere, but, unlike a sphere of hard material, it flows radially at very high velocity during the collision. Because it acts like a hard sphere, it exerts a compressive impact load at the point



Flat Specimen after 25 sec

Flat Specimen after 1 min

Flat Specimen after 5 min

Airfoil Specimen after 5 min

FIGURE 5. EFFECT OF SPECIMEN SHAPE ON THE RAIN EROSION RESISTANCE OF NYLON FM-10001. STUDY III. SCALE DIVISIONS ARE mm.

of the collision; because it flows radially it imposes shear and tensile stresses on the surface layers of the solid material and exerts a turning power against any protrusion of the solid material above the planar surface of it. The waterdrop always imposes the same stresses. Whether or not erosion occurs on the surface of a solid material that the waterdrop strikes at any arbitrary velocity, and the course that the erosion takes if it does occur, depend on the properties of the solid. There are, consequently, as many different mechanisms of erosion as there are broad groups of structural properties. If the properties of a single substance can be varied, there will be more than one mechanism possible by which rain erosion can be produced on it. Such a change in properties is especially easy to accomplish in the case of plastics materials, and if this fact is not considered in preparing specimens, rain erosion test results on materials of this kind will be unpredictable and misleading.

Comparison of the degree of damage produced in Study II and Study III for the same waterdrop impingement velocity and rain rate and for the same time of test on the same plastics material is convincing evidence of the importance of this fact. Two pairs of eroded specimens, one pair after 5 min of test and one pair after 30 min of test, are shown in Figure 6. It can be seen from these pictures that a durable rain-erosion-resistant material, such as nylon FM-10001 has proved itself to be by the erosion resistance of the specimens of Study III, could be completely misjudged on the basis of the behavior of specimens such as those of Study II, which were not representative of the original plastics material. To recapitulate, the specimens of Study II contained the residual stresses that were present in the sheet material from which they were formed. These stresses produced surface crazing which made the specimens subject to the turning power exerted by the radial flow of water from the impinging drops and resulted in the rapid breaking away of material between the craze cracks. The specimens of Study II had also been exposed to excessive heating during forming. This resulted in a discolored surface layer that may have been embrittled and which was quickly broken off by the impinging drops just as a thin brittle coating is rapidly broken off. The roughened surface that was left made the specimen more vulnerable to the waterdrop blows because of the pressure multiplication that occurs in irregular surface depressions as well as in pits. The specimens of Study II also contained stresses that were introduced during the forming operation itself. These stresses later caused a change in shape of the specimens. The layer of material on the outer surface of the specimens was stretched in tension and material that is already in tension should fail more easily under an applied tensile load than could be expected for

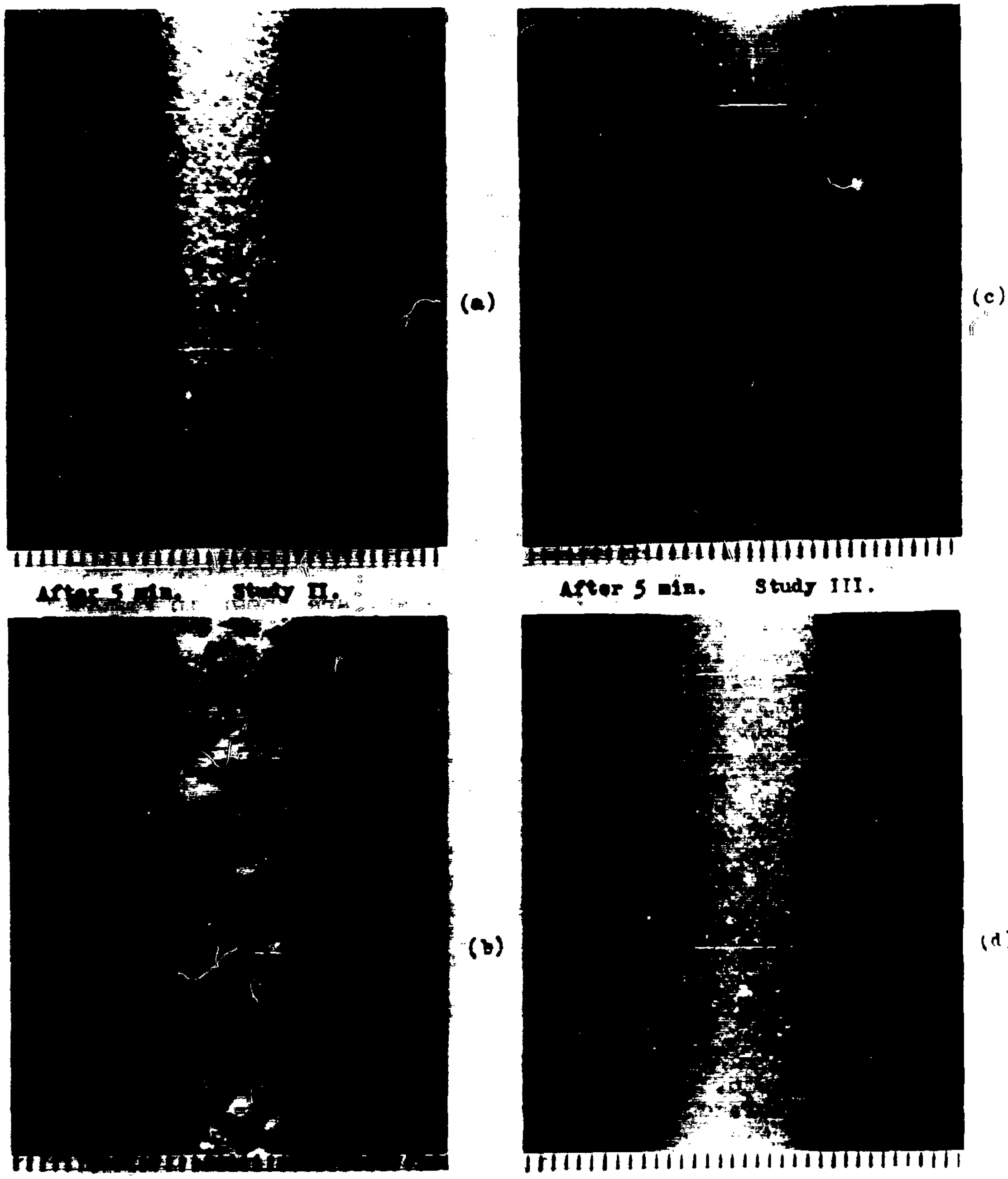


FIGURE 6. EFFECT OF RESIDUAL STRESSES AND OF MOLDING VARIABLES ON THE RAIN EROSION RESISTANCE OF [illegible]-10001. SCALE DIVISIONS ARE mm.

unstressed material. For these reasons the progress of erosion on the specimens of Study II and the mechanism by which it occurs is fictitious as far as nylon FM-10001 in its optimum state of strength is concerned.

It is possible that even greater rain-erosion resistance may be shown by nylon FM-10001 than has been shown by the specimens of Study III. The fact that there was a change in shape of these specimens after they were molded shows that residual stresses existed in them. As was noted in Section 3.1, there are at least two ways by which the introduction of these stresses may have occurred. The specimens may have been molded before the interior and exterior layers of the nylon sheet material from which they were made had reached temperature equilibrium, so that the interior layers were molded before they had reached the correct forming temperature for the pressure that was applied. On the other hand, it may be a time effect; more time may be required than was allowed for the polymer chains to move into their new positions in the molded specimens. If the deformation results from the failure to establish temperature equilibrium, the nylon sheet should be placed in the oil bath when it is cold and should be brought up to the 400°F-molding temperature with the oil. If the nylon sheet is put into the oil bath when it is hot, it should be kept there at a temperature of 350-375°F for as long as 15 min before the specimens are raised to 400°F and formed. If a time effect is involved in the deformation of the molded specimens, then the specimens should be heated in the mold after forming at a temperature of 350-375°F for 30 min or longer before a very gradual cooling of the mold to room temperature is permitted.

It is possible that even more is involved in the marked improvement of the rain erosion resistance of the nylon specimens of Study III over that of the nylon specimens of Study II than simply the removal of residual stresses in the original sheet material by prior heat treatment or than avoiding the deterioration of the surface layers of the specimen by excessive heating. Nylon is a plastics material that is partly crystalline. The properties of it are determined by the proportion of crystalline to amorphous matter that it contains (7). The degree of crystallinity that exists in a specimen of this material is determined by its previous history. The crystallites of high polymers are submicroscopic bodies that are attached to adjacent amorphous matter by covalent bonds (8). Spherulites of high polymers are partially oriented groups of crystallites and their attached amorphous matter which appear to result from approximately radial growth away from a single nucleating crystallite (8). If crystallization is given time to take place at a sufficiently high temperature to obtain heterogeneous nucleation with a minimum of homogeneous nucleation, a relatively small number of nuclei will grow into spherulites at the low rate that is characteristic for the process at high temperature (8). Large spherulites of uniform size are obtained in this way, and their slow rate of growth probably favors greater perfection (8). Rapid spherulite growth in the range of homogeneous nucleation, which occurs at a lower temperature, is favored by the lower temperature (8). In this temperature range a large population of nuclei grow rapidly to produce small spherulites, and the over-all crystallinity of the product is likely to be lower (8).

With regard to polyamides, slow cooling produces a stiff and hard solid which is predominantly crystalline in structure; rapid cooling of the melted polyamide results in a highly amorphous product (7). In consideration of these facts, it is possible that the prior heat treatment given by the manufacturer to the sheet material that was used for the specimens of Study III had induced a higher degree of crystallinity in it than existed in the material used for the specimens of Study II. Likewise, from these considerations, it is also possible that an even higher degree of crystallinity can be induced in specimens if they are held at a temperature of 350-375°F for 30 min or longer after forming and if they are cooled to room temperature at an even slower rate. It is possible that the rain erosion resistance of nylon FM-10001 may be shown to be even greater than that displayed by the specimens of Study III if this heat treatment is given to the molded specimens before they are tested.

It is also known that internal stresses in polyamides are relieved by after-treatment, especially in the presence of water, and that surface hardness is increased (9). The increase in surface hardness may be due to increased crystallinity on the surface. It has been stated that water acts as a plasticizing agent in nylon, possibly by loosening hydrogen bonds, and hence allows readjustment of the crystal structure to occur (10). On the basis of this information, it is possible that heat treatment of the specimens in water or steam after the forming process is complete may further increase their rain-erosion resistance. It is possible that the rain erosion resistance of nylon FM-10001 can be made even greater by use of an after treatment of this kind.

The strength properties of nylon FM-10001 that have been determined by test and the resistance that this material has shown to the impingement of deforming lead pellets both indicate that it should be a close approach to the rigid-material solution of the rain erosion problem at an impingement velocity of 600 mi/hr. A further study of nylon is planned to determine as far as possible the maximum rain erosion resistance of this material and to obtain more evidence in regard to the mechanism by which it eventually fails.

Note added in revision:

Evidence of a cementitious deposit has been observed on specimens that were tested at a velocity of 600 mi/hr on the Cornell Aeronautical Laboratory rotating arm in simulated rain. The simulated rain is made with use of city water that is recycled for use in the erosion tests. It appears that hardness in the water is precipitated during the high speed collision of the specimen with the drops of water. A preliminary investigation of why this precipitation occurs has indicated that it may result from a boiler-scale type of reaction due to transformation of kinetic energy into heat during the high speed collisions between the moving specimen and the waterdrops. The amount of precipitation that occurs appears to be much less at an impingement velocity of 500 mi/hr than at an impingement velocity of 600 mi/hr.

The presence of precipitated hardness in the water enhances the abrasive action of the radial flow of the waterdrops after collision; it adds a concomitant grit abrasion to the high speed rain erosion test. In the case of nylon it may have caused surface scratching and (or) the scraping up of thin tendrils of surface material and in this way it may have influenced the final erosion test results and the deductions made from inspection of the eroded specimens.

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